

6 Recommendations

California's routine databases on emissions and ambient air quality are uncommon in their extent and their quality. In addition, many special studies that address air quality issues have been conducted in California. Data from these sources have already answered many questions concerning the ozone weekend effect. However, the objectives of routine programs and special studies have not specifically included understanding day-of-week differences in ozone and other pollutants. It is not surprising, therefore, that explaining the ozone weekend effect will require additional information to augment existing databases.

This chapter presents a multi-disciplinary research program needed to resolve the cause(s) and implications of the ozone weekend effect. Without this effort, the cause(s) and implications may remain ambiguous.

6.1 Recommendations for further research

The recommendations in this section identify information needed to resolve the causes of the ozone weekend effect. Several hypotheses in this regard are discussed in Chapter 3 of the Staff Report. However, the data available for the analyses included in this report were not sufficient to separate or quantify the contributions of the various causes. Without the research outlined here, the relative importance of these hypothetical causes will be difficult to resolve. This section integrates and extends recommendations given in earlier chapters and presents unified recommendations to guide future work.

6.1.1 Summary of recommendations

The search for the cause(s) of the ozone weekend effect involves several questions, and these questions must be answered for each day of the week. What compounds exist in the atmosphere and in what quantities? How and where are these materials emitted or formed? How do these materials interact to produce ozone? How do we collect and analyze data to answer these questions? The recommendations that follow address these questions.

- **Improved data on ambient air quality**

Existing databases for ambient air quality must be augmented in several respects before the alternative cause(s) of the ozone weekend effect can be resolved. An expansion of routine sampling methods alone will not suffice. Instead, a major field study in the South Coast Air Basin is recommended to gather the necessary ambient air quality data.

- **Improved emission inventories**

Emission inventories for each day of the week are needed to help determine the causes of the ozone weekend effect. In particular, day-of-week emission inventories are needed to support air quality models that simulate the ozone weekend effect. Separate inventories for Saturday and Sunday are essential. Although desirable, separate inventories for individual weekdays may not be feasible.

The required inventories must reveal in sufficient detail the quantity, the timing, and the location of VOC and NO_x emissions by day of week. Day-specific hourly emissions are needed for stationary and area sources as well as for mobile sources.

- **Improved modeling**

Modeling exercises would use new day-specific inventories to investigate how the mix of primary and secondary pollutants affects ozone formation on weekdays and on weekends.

Dynamic simulation models such as the Urban Airshed Model (UAM) are important tools for comparing alternative strategies for reducing emissions. Modeling exercises should be used to compare and contrast the effects of periodic emission reductions on weekends to the effects of strategic emission reductions on all days. Only models can make such comparisons because the strategic reductions of interest have not yet occurred.

- **Improved information from laboratory experiments**

Earlier experiments would be updated based on present-day conditions in the SoCAB. New experiments would be conducted to address important alternative causes of the ozone weekend effect.

Many past experiments have already revealed important aspects of ozone-producing systems. However, these experiments were often designed from a generic perspective, and they may not be directly applicable to the ozone weekend effect. These experiments should be repeated based on the conditions found during the air quality studies recommended above.

6.1.2 Conduct a field study to augment the existing ambient air quality databases in the South Coast Air Basin

Existing databases for ambient air quality are inadequate to resolve the cause(s) of the ozone weekend effect. Despite extensive analyses by the ARB staff and others, the relative importance of the alternative causes outlined in Chapter 3 of the Staff Report cannot be determined. Air quality data must be more precise (accurate), more specific (artifact-free), and more extensive in

time (hourly) and space (three-dimensional). In addition, detailed observations must be available for multiple weekday-weekend transitions comprising Friday to Saturday to Sunday to Monday rather than for “episodes.”

Therefore, a major field study is recommended to gather the ambient air quality data needed to bridge the significant gaps in the data. An outline for the recommended study is presented here as a starting point for further discussion and planning.

6.1.2.1 Requirements for routine and intensive sampling periods

To obtain a sufficient overall database, 18 months of continuous sampling at surface sites is recommended. Beginning in May of one year and ending in October of the following year, the study would cover two ozone seasons and one winter. Sampling in May and October is important because existing research suggests that the ozone weekend effect may differ in spring, summer, and fall. Sampling during the winter is needed to support research on weekday-weekend differences in fine particulate matter (PM_{2.5}) and other pollutants that are important health concerns during the winter months.

Air quality sampling in support of research on the ozone weekend effect will require intensive sampling on more days than most other field studies. Studies such as SCAQS87 and SCOS97 included intensive sampling operations on less than 20 days each, which was sufficient to acquire episodes for modeling representative “peak days” but was not sufficient to address the ozone weekend effect.

The ozone weekend effect is embedded in the differences in ozone and its precursors for each day of the week. All seven days are important, with weekday-weekend transitions being most important. Furthermore, most days in an ozone season, rather than just a few episode days, will contain relevant information. A transition from 70 ppb ozone on Friday to 90 ppb on Saturday can be just as revealing as a transition from 140 ppb to 160 ppb.

It is particularly important to sample days in sequence so that Fridays can be compared to adjacent Saturdays, etc. In the combined data from 34 intensive sampling days during SCAQS87 and SCOS97, there are just four transitions from Friday to Saturday, one transition from Saturday to Sunday, and one transition from Sunday to Monday.

Intensive sampling involves measurements of pollutants aloft (see paragraph 6.1.2.4 below) in addition to the continuous surface measurements. These data are needed to characterize the size, composition, strength (concentrations), duration, and frequency of reservoirs of polluted air aloft. To do this, a minimum of 8 intensive periods of 4 days each are needed, making a total of 32 intensive sampling days. Each four-day sequence must include Friday, Saturday, Sunday, and Monday.

6.1.2.2 Data quality

Highly accurate and reliable data are needed to identify and quantify the alternative causes of the ozone weekend effect. Therefore, measurements would be made using state-of-the-art, artifact-free methods that can be deployed in the field.

Thorough QA/QC procedures should be applied to assure the validity of all data. The QA/QC procedures should include representative co-located monitoring at two or more locations for each type of data.

6.1.2.3 Requirements for air quality sampling at the surface

6.1.2.3.1 Resolution in time

For air quality measurements at the surface, hourly resolution is feasible and should be sufficient for all compounds of interest. Measurements at longer time intervals are significantly less useful and should not be pursued.

6.1.2.3.2 Resolution in space

In each air basin to be considered, data are needed at sites representing source regions, at sites representing receptor regions, and at sites that help discriminate between alternative causes of the ozone weekend effect. The sites representing these categories may shift under differing meteorological conditions.

In the South Coast Air Basin (SoCAB), seven to twelve locations are recommended to provide sufficient spatial coverage. One to three upwind, coastal sites would be drawn from Costa Mesa, Hawthorne, N. Long Beach, and West L.A. Two or three central source sites would be drawn from Anaheim, Burbank, L.A. – N. Main, Lynwood, Pasadena, and Pico Rivera. Two or three downwind receptor sites would be drawn from Lake Elsinore, Lake Gregory, Riverside, San Bernardino, and Santa Clarita. Finally, two or three transitional (discriminating) sites would be drawn from Azusa, Reseda, and Upland. For other air basins, a similar mix of sites would be selected.

A set of nine sites with intermediate spatial resolution is the following:

Coastal: N. Long Beach and West L.A.

Central: Anaheim, L.A. – N. Main, and Lynwood

Downwind receptors: Lake Gregory and Santa Clarita

Transitional: Reseda and Upland.

6.1.2.3.3 Required pollutants

Measurements of the following pollutants are needed:

6.1.2.3.3.1 Aggregate hydrocarbons

Hourly measurements for the duration of the field study are needed for total non-methane organic compounds (TNMOC). Understanding the ratio of TNMOC (or VOC) to NO_x is crucial for discriminating between alternative causes of the ozone weekend effect. Hourly hydrocarbon data are needed to better characterize rapid changes in concentrations (e.g., morning mixing processes) and diurnal variations, particularly in relation to hourly changes in VOC/ NO_x ratios. The 3-hour interval in the PAMS program is too coarse for these purposes. In addition, it has been reported that the PAMS data may underestimate the total VOCs by 30 percent or more.

Currently, a joint ARB/SCAQMD project has three TECO 55 C instruments collecting TNMOC data at Anaheim, L.A. – N. Main, and Lynwood. Additional instruments, presently in use for the Central California Ozone Study, may be available to deploy at four to nine additional locations for the recommended study.

6.1.2.3.3.2 Speciated hydrocarbons

Measurements of selected hydrocarbon species are needed in addition to the aggregate TNMOC data. The standard set of compounds measured in the PAMS program is minimally sufficient. Additional compounds should be included if they will help discriminate between alternative causes of the ozone weekend effect.

Hourly measurements of speciated hydrocarbons are not needed for every day of the field study. Measurements are needed in sufficient quantity to note significant differences between hourly profiles by day-of-week. It is possible that 24 (hourly) samples on 10 days for each day of the week (70 days total) would be sufficient for this purpose.

6.1.2.3.3.3 Compounds containing nitrogen

Routine measurements of NO_x partially represent “ NO_Y ”, which includes several nitrogen-containing compounds in addition to NO and NO_2 . The compounds that are partially captured include PAN, gaseous nitric acid, nitrate particles, and N_2O_5 , among other reactive compounds containing nitrogen. Routine methods for NO_x measure a portion of these important compounds in aggregate rather than separately.

Routine NO_x data are available at many locations but these data lack the precision as well as the specificity needed to obtain accurate estimates of

important ratios. For example, VOC/NO_x , O_3/NO_y , and NO_2/NO may help show which alternative causes of the ozone weekend effect are important. Progress in understanding the ozone weekend effect is unlikely without state-of-the-art measurements for nitrogenous compounds.

6.1.2.3.3.3.1 NO_x

Nitrogen oxides, or NO_x , is a major concern of weekend effect research. According to the NO_x -reduction hypothesis, the ratio of VOCs to NO_x is the dominant factor determining the ozone weekend effect. The ratio of NO_2 to NO is also a factor in NO_x -timing hypothesis. The ratios of O_3 to NO_y aloft may indicate whether conditions there are mostly NO_x -limited or VOC-limited.

Conventionally, the term NO_x refers to the sum of NO and NO_2 . However, routine measurements for NO_x have two drawbacks, as noted above. First, the routine method lacks specificity since compounds such as gaseous nitric acid (HNO_3) and peroxy-acyl-nitrates (PAN) can interfere and appear as NO_x to the instrument. Second, the routine method cannot quantify NO_x accurately at very low concentrations. Relatively recent advances in monitoring methods have overcome both of these limitations.

Accurate and specific measurements of NO and NO_2 are needed hourly throughout the duration of the study to help resolve the cause(s) of the ozone weekend effect.

6.1.2.3.3.3.2 Total reactive nitrogen: NO_y

Total reactive nitrogen, or NO_y , is the sum of NO_x , gaseous nitric acid, PAN, nitrate particles, and other reactive compounds that contain nitrogen. NO_y is an important part of analyses that concern the ozone weekend effect.

The ratio O_3/NO_y can help indicate whether a photochemical system is in a VOC-limited or NO_x -limited condition. It has been suggested that low concentrations of NO_y alone may indicate NO_x -limited conditions. The concentration of NO_y may be a crucial factor when assessing the impact of carryover aloft on ozone formation.

Accurate and specific measurements of NO_y are needed hourly throughout the duration of the study to help resolve the cause(s) of the ozone weekend effect.

6.1.2.3.3.3.3 Total reacted nitrogen: NO_z

The total reacted nitrogen, or NO_z , is equal to $\text{NO}_y - \text{NO}_x$. The slope of a line relating ozone (ppb) to NO_z (ppb) has been called the "ozone production efficiency." This parameter may be helpful in assessing the role of the NO_x -timing hypothesis in the ozone weekend effect. According to this hypothesis, the timing of NO_x emissions on weekends causes the smaller amount of NO_x

on weekends to be more efficient in producing ozone compared to the larger amount of NO_x on weekdays.

Because NO_z is NO_y minus NO_x , high quality NO_z data depends on the collection of high quality NO_x and NO_y data.

6.1.2.3.3.4 Nitric acid: HNO_3

Gaseous nitric acid, $\text{HNO}_3(\text{g})$, has been used in relation to hydrogen peroxide to discriminate between VOC-limited and NO_x -limited photochemistry. In addition, the nitric acid concentration can indicate the rate at which nitrogen-containing compounds are removed from the ozone-producing system. The faster nitrogen is removed, the faster the atmosphere changes from a VOC-limited condition to a NO_x -limited condition. The timing of this transition on different days of the week may be an important factor in assessing the contributions of several hypotheses.

Accurate and specific measurements of $\text{HNO}_3(\text{g})$ are needed in sufficient quantity to note significant differences between hourly profiles by day-of-week. It is possible that 24 (hourly) samples on 10 days for each day of the week (70 days total) would be sufficient for this purpose.

6.1.2.3.3.5 Peroxy-acyl-nitrates: PAN

Peroxy-acyl-nitrates, or PAN, is a family of compounds that are notoriously difficult to measure. These compounds contain two parts, an organic radical and NO_2 . PAN has been identified as a source of both NO_2 and reactive organic species in polluted air masses transported long distances. PAN may also be an important indicator of the impact of carryover, especially carryover aloft.

Accurate and specific measurements of PAN are needed in sufficient quantity to note significant differences between hourly profiles by day-of-week. It is possible that 24 (hourly) samples on 10 days for each day of the week (70 days total) would be sufficient for this purpose.

6.1.2.3.3.4 *Other species*

If reliable and accurate methods are available to measure nitrous acid (HONO), hydrogen peroxide (H_2O_2), hydroxyl radicals ($\cdot\text{OH}$), and nitrate radicals ($\cdot\text{NO}_3$) these species should be included on enough days to provide useful contrasts between weekdays and weekends.

Data for elemental carbon (black particulate matter) and solar radiation should be collected at each surface site. These data are necessary to assess the importance of the “soot and sunlight” hypothesis concerning the impact of ultra-violet radiation on the ozone weekend effect. According to this

hypothesis, vehicular activity is much lower on weekends resulting in large reductions in elemental carbon. With less black particulate matter, less UV radiation is absorbed and more UV radiation is available to initiate the photochemical reactions that lead to ozone.

6.1.2.4 Requirements for measurements aloft

Data from the 1997 Southern California Ozone Study (SCOS97) and other field studies indicate that layers of polluted air sequestered aloft can contain high concentrations of aerosols and ozone. Furthermore, such layers aloft may be routine rather than unusual. These observations indicate that conditions aloft are not simply a homogeneous mixed layer trapped below a temperature inversion.

An extensive measurement program is necessary to determine the frequency and persistence of polluted layers aloft, to quantify the pollutants contained in such layers, to evaluate diurnal patterns aloft, and to quantify how surface concentrations are affected. Measurements aloft are required for a minimum of 15 weekday-weekend transitions, that is, Friday to Saturday to Sunday to Monday. This means a total of 60 days for collecting samples aloft.

6.1.2.4.1 Resolution of measurements aloft in time and space

It is not feasible to acquire some types of data aloft with the same high resolution that is feasible at the surface. For example, an ideal sampling plan might call for measurements every 100 meters between the surface and 1500 meters for each hour. At this resolution, the data collected aloft would be 15 times as much as the surface data for the same period. Although compromise may be necessary, the study design must remain sufficient to achieve the goals.

Horizontally, measurements aloft should characterize a minimum of four locations – a central location and three surrounding locations. The geographical orientation of the South Coast Air Basin suggests the need for five locations. These five locations are the following: (central) San Gabriel Valley, (northwest) San Fernando Valley, (west) downtown L.A., (south) Orange County, and (east) Riverside or San Bernardino County. Specific locations might be Cal Poly-Pomona, C.S.U.-Northridge, UCLA, U.C.-Irvine, and U.C.-Riverside.

Vertically, measurements aloft should be collected with enough resolution to characterize the important layers and their interactions with pollutants at the surface. One design that may be satisfactory would gather integrated samples, one between 100 and 200 meters, one between 200 and 500 meters, and another between 500 and 1000 meters. Alternatively, measurements might be taken at heights based on significant changes in temperature or humidity.

Hourly measurements aloft are highly desirable but may not be feasible for the 60 days required. Instead, it may be satisfactory to sample hourly during daylight hours, with less frequent sampling during the remaining hours. Some nighttime sampling is vital for determining the identity and quantity of pollutants that carry over aloft.

6.1.2.4.2 Methods

Aircraft, balloons, towers, and other means may be used to gather the needed data aloft. Remote sensing instruments (e.g., LIDAR) would allow some measurements to be sampled densely in space and time.

Sampling methods used aloft should provide accuracy and precision similar to the sampling methods used for surface measurements.

6.1.2.4.3 Pollutants

Measurements aloft should include the same spectrum of pollutants as measured at the surface if possible.

6.1.2.4.4 Tracers

The proportional contributions of fresh emissions from the surface and aged emissions from aloft may be crucial to a proper understanding of the ozone weekend effect. Tracers might be used to increase our understanding in this area. Tracers aloft and subsequently measured at ground level might help attribute the surface concentration of a pollutant to fresh emissions from the surface and to aged emissions from aloft in the proper proportions.

This information is needed to help evaluate the validity of the “carryover aloft” hypothesis.

6.1.3 Analyses of the ozone weekend effect in other regions

For the most part, this report focuses on results of analyses concerning the South Coast Air Basin. One naturally asks, “What do similar analyses show in other regions of California?” Some of the technical chapters recommend such analyses. At this time, however, extensive investigation of other regions is not recommended. Lack of data is the reason.

The SoCAB is relatively rich in the extent and variety of their data. Nevertheless, the data were inadequate to resolve key issues. The dense monitoring network was encouraging, but very few locations collected crucial hydrocarbon data. The rich database for freeway traffic was interesting, but the data did not include surface streets and did not resolve light-duty and heavy-duty activity by hour. WIM classification data were helpful, but the number of sites is limited and the data were 24-hour aggregates rather than hourly. More in-depth field studies have been carried out in the SoCAB than

any other basin, but the available data on air quality aloft are inadequate for the present task.

Despite the generous sources of data in the SoCAB, the analyses were inconclusive. Therefore, analyses in other regions should be carried out only when the required data are available. Otherwise, valuable resources are likely to purchase nothing but additional inconclusive results.

6.1.4 Develop day-specific emission inventories to support efforts to model weekday-weekend differences in ozone

Day-of-week hourly emission inventories are needed to support UAM simulations of the ozone weekend effect. To date, day-of-week emission inventories used in modeling exercises have been largely speculative. Day-specific hourly emissions are needed for mobile, stationary, and area sources.

The following recommendations address work already planned or in progress and work that may be needed in addition to present plans.

6.1.4.1 Acquire and analyze hourly data for on-road vehicle activity by vehicle class throughout the SoCAB.

The traffic analyses presented in Chapter 5 were lacking in at least four ways. First, the data did not include freeways in the Riverside and San Bernardino County portions of the SoCAB. Second, the hourly freeway data for Los Angeles and Orange Counties were not separated by vehicle class. Third, no data for surface street activity were considered for any part of the SoCAB. Fourth, the WIM classification data were not hourly. The recommendations that follow address these issues.

6.1.4.1.1 Acquire and analyze freeway traffic counts for Riverside and San Bernardino Counties

For this report, no freeway traffic data were available east of Pomona (Los Angeles County). Emission inventories in Riverside and San Bernardino Counties are important because these areas are usually downwind receptors with respect to emissions from L.A. and Orange Counties. Fresh local emissions of VOCs and NO_x may alter the photochemistry that would otherwise occur for the aged and transported emissions.

Sub-domains similar to those used in Chapter 5.2 should be identified. These sub-domains could be centered on the monitoring sites located at Fontana, Lake Elsinore, Lake Gregory, Redlands, Riverside, San Bernardino, and Upland. For each sub-domain, hourly vehicle counts on the freeways should be obtained.

6.1.4.1.2 Acquire hourly data from WIM stations and use these data to disaggregate hourly freeway data by vehicle class

The California Department of Transportation (CALTRANS) maintains a limited network of Weigh-in-Motion (WIM) stations on state highways. These stations can provide important information on weekday-weekend differences in the volume and composition of traffic. Each station collects hourly data on the frequency of vehicles in 14 different vehicle classes. Hourly traffic data is important because it can be compared more effectively with hourly data on ambient air quality. The WIM data analyzed for this report were provided as daily rather than hourly summaries.

Plans are already in place for ARB and CALTRANS staff to cooperate in preparing and analyzing retroactive hourly traffic data from all of the WIM stations relevant to the SoCAB. The period of interest is June through October 1997, bracketing the SCOS97 field study. Plans call for these data to be used to disaggregate the hourly freeway counts for Los Angeles and Orange Counties by vehicle class.

When available, hourly activity data for freeways in Riverside and San Bernardino Counties could also be disaggregated using the WIM data. For this purpose, data from the WIM stations east of Pomona should be used.

6.1.4.1.3 Acquire and analyze hourly summaries for vehicle activity by class on surface streets throughout the SoCAB.

Approximately half of the total vehicle miles traveled in the SoCAB occur on freeways; the remaining VMT occur on surface streets. Vehicle activity data for surface streets are less readily available compared to freeway data. Nonetheless, these data are needed to complete the picture of on-road motor vehicle activity by hour and day of week in the SoCAB.

Hourly traffic counts on surface streets by vehicle class are needed throughout the SoCAB. At least three vehicle classes – light-duty, medium-duty, and heavy-duty – should be supported.

Data should be gathered in each of the eleven sub-domains identified in Section 5.2 of this report. Additional sub-domains of Riverside and San Bernardino Counties should also be included. The existing air quality monitoring stations at Fontana, Lake Elsinore, Redlands, Riverside, San Bernardino, and Upland could be used as center-points for sub-domains of Riverside and San Bernardino Counties.

In each sub-domain, hourly data should be collected for a representative sample of surface street locations for a minimum of four complete weeks.

6.1.4.1.4 Update analyses that were based on 1997 traffic data to synchronize them with analyses of more recent data

It may be not be necessary to synchronize the analyses of traffic data. For example, hourly traffic profiles from 1997 may be satisfactory for some time to come. If significant doubts arise, however, the earlier analyses of 1997 traffic data should be updated using concurrent data.

6.1.4.2 Quantify WD/WE emission differences for important stationary-source and area-source categories

Emissions from some categories of stationary-sources and area-sources may be substantially different on weekends compared to weekdays. A two-stage effort is recommended. First, identify significant stationary-sources and area-sources that are likely to operate differently on weekends compared to weekdays. Second, gather sufficient information to characterize the activity levels of these sources by hour by day-of-week.

This effort should focus on the SoCAB first and other air basins as resources and priorities allow.

6.1.4.2.1 Identify important categories

The search for important categories of stationary-sources and area-sources begins with categories that emit a significant fraction of the total VOC or NO_x emissions. For comparison to mobile source categories, on a weekday in the SoCAB in 1995, trucks emit approximately 16% of the total NO_x emissions from all sources, while fuel combustion at stationary sources accounts for approximately 10% of the total.

The search continues by selecting those categories that are likely to operate differently on weekends compared to weekdays. Important differences may include quantitative changes in activity and qualitative changes in activity, such as a change in location.

6.1.4.2.2 Collect information needed to characterize emissions by hour by day-of-week for the important categories

The current structure for the emission inventory for stationary sources reserves space for codes that indicate the days of operation per week and the hours per day when operating. This information would provide a basis for constructing day-specific hourly emission inventories. However, many districts have not yet reported the facility information needed to fill the space reserved.

For the important source categories, the needed data to construct satisfactory day-specific hourly inventories should be collected.

6.1.4.2.3 Analyze existing data from continuous monitoring of major industrial sources of NO_x emissions

During the last decade, many major industrial sources of NO_x emissions installed “in-stack” or continuous emissions monitoring (CEM) systems. Facilities in several source categories may qualify, including oil refineries, electric utilities, co-generation facilities, and others requiring high-temperature fuel combustion.

The plumes from these sources are buoyant due to their high temperature and tend to inject NO_x emissions into polluted layers aloft. In the morning, surface measurements are not likely to capture NO_x from buoyant plumes. Day-of-week comparisons of NO_x measurements aloft with activity profiles for sources with buoyant plumes may be an important factor in understanding the ozone weekend effect.

Day-of-week emission profiles for NO_x from facilities with CEM should be constructed. The relationship between facilities with CEM and without CEM should be evaluated to see whether the emission profiles can be applied to both categories.

6.1.5 Design and execute modeling studies of the ozone weekend effect

Dynamic simulation models such as the Urban Airshed Model (UAM) are important tools for comparing alternative strategies for reducing emissions. These models can simulate the effects of changes in emissions that have not yet been experienced in the real world.

Effective and reliable simulations require satisfactory agreement between model predictions and appropriate “base case” conditions. The modeling exercises recommended here should not be carried out until such a base case has been developed based on the air quality and emissions activity data recommended above. When satisfactory base cases characterizing day-of-week emissions are available, a carefully designed series of modeling exercises should be run. These exercises should address all of the alternative hypotheses concerning the cause(s) of the ozone weekend effect.

The Coordinating Research Council and the National Renewable Energy Laboratory currently have a contract with ENVIRON to carry out a series of modeling exercises related to the ozone weekend effect. However, these exercises are relying on the same inventories that we consider to be in need of significant improvement. The framework for these exercises and the results should be fully considered before further exercises are designed and executed.

The results of the UAM exercises should be compared to the ambient data and to the results of selected laboratory experiments, such as those described in the next section.

6.1.6 Laboratory Experiments Update and extend laboratory data concerning alternative causes of the ozone weekend effect

Scientists have carried out many useful experiments that reveal aspects of ozone-producing systems. These experiments are often designed from a generic perspective instead of a location-specific perspective. Some of these classic experiments should be repeated using conditions specific to those found during the air quality sampling discussed above. In addition, new experiments should be done to isolate important points that may discriminate between the alternative hypotheses described in Chapter 3 of the Staff Report.

6.1.6.1 Evaluation of model accuracy when VOC/NO_x ratios are low

When VOC/NO_x ratios are in the neighborhood of five, chemical mechanisms contained in some models may fail to generate enough ozone to match experimental observations. Because the VOC/NO_x ratio is a crucial factor in the NO_x-reduction hypothesis, laboratory experiments should be done to assess the accuracy of model predictions when VOC/NO_x ratios range from four through twelve.

6.1.6.2 Evaluation of model accuracy under low NO_x conditions

Under “low NO_x” conditions, such as may occur during the early daylight hours on Saturday and Sunday, chemical mechanisms contained in some models may generate too much ozone. Some models and some laboratory experiments indicate that the “reactivity” of VOCs generally decrease as the concentrations of NO_x decrease. Appropriate comparisons of laboratory results and model results should be made.

6.1.6.3 Evaluation of NO_x-timing effects

Experiments conducted by Hess, et al., considered some effects of NO_x timing (cf. references for Chapter 3 of the Staff Report). These experiments did not always use real-world conditions because their purpose was to emphasize differences between alternative chemical mechanisms used in UAM-style models. Nevertheless, the experiments indicated that fresh NO injected around mid-day may cause a large increase in ozone.

When applied to the ozone weekend effect in the SoCAB, the experiments by Hess, et al. have a potentially important drawback. The experiments used initial VOC/NO_x ratios from 15 to 50. In the SoCAB, measured VOC/NO_x ratios at the surface are generally between 5 and 10. In addition, the experiments may have used profiles for VOC species that were substantially different from those that prevail in the SoCAB.

Selected laboratory experiments that alter the timing and the amount of NO_x emissions should be carried out. These experiments should use conditions that reflect the best available data for VOCs and NO_x in the

SoCAB. The chief focus of these experiments is to assess the plausibility of the NO_x-timing hypothesis.

6.1.6.4 Laboratory evaluation of the effects of carryover aloft

The effect on surface ozone concentrations of materials that carryover aloft is an important question for further research. If possible, smog chamber experiments should be used to investigate the effects of “aged,” ozone-rich air on the ozone production of fresh emissions.

Earlier experiments have considered dilution effects and some timing effects. Dilution, however, has been explored using clean air to dilute contaminated air such as that found near the surface. Dilution experiments should be carried out in which the air used to “dilute” contains materials that simulate the air that may carryover aloft.

